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13. ABSTRACT (Maximum 200 words)  Catalysts using Ag+ and Fe2O3 as dopants on sodalite, Y zeolite and MCM-41 supports were investigated in order to develop a more efficient and safe catalyst for the photodecomposition of dangerous nerve agents. Ag-sodalite, Ag/Fe2O3-sodalite, Ag-Y zeolite, Ag-MCM-41 and Ag/Fe2O3-Y zeolite were all synthesized by ion exchange techniques and characterized by X-ray diffraction, solid state luminescence spectroscopy, and atomic absorption spectroscopy. The Y zeolite-based catalysts show significant spectroscopic differences between the Ag-doped and the Ag and Fe2O3-doped varieties. Catalyst performance studies involving each of the synthesized catalysts were conducted using carbaryl as the reactant and varying wavelengths of UV light as photon sources for the experiments. Catalyst performance studies were also carried out use nerve agents as the target molecules at the Edgewood Chemical and Biological Center. While catalysts perform differently depending on the excitation wavelength used, the Ag-sodalite catalyst at 280 nm excitation shows the most promise for its efficiency and stability. Also, the inclusion of Fe2O3 as a dopant does not enhance catalytic activity. Reactions using Ag-sodalite at 280 nm excitation involving either sodium bicarbonate as a hydroxyl radical scavenger or D2O as solvent show that hydroxyl radicals may play a role in the reaction mechanism.				
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# **Development of a Rapid Decontamination System for Nerve Agents: Final Report**

## **Table of Contents**

Statement of Problem Studied	2
Catalyst Synthesis and Characterization	2
Reactor Design	4
Experiments Involving Nerve Agent Simulants	6
Experiments Involving Nerve Agents	9
Publications and Reports Resulting From Research	11
Participating Scientific Personnel	11
Bibliography	12

## **List of Figures and Tables**

Table 1. Zeolite catalyst types	2
Figure 1. Three-dimensional excitation spectra of fully exchanged silver zeolite Y at 77K	3
Figure 2. Solid state luminescence excitation spectra at 77K of (left) Ag-Y Zeolite and (right) Ag/Fe-Y Zeolite	4
Figure 3. Automated batch reactor aligned with a tunable UV laser source	5
Figure 4. Assembled photo-activation device	6
Figure 5. Averaged quantum yields for each of the synthesized catalysts for three different excitation wavelengths	7
Figure 6. Luminescence intensity of carbaryl over time in the presence of Ag- sodalite and 280 nm excitation under differing conditions	8
Table 2. Nerve Agent Breakdown Results	9

## Statement of the Problem Studied

This research was undertaken in an effort to develop a non-toxic photocatalytic decontamination technology based on silver-exchanged zeolites for the potential application of destruction of chemical warfare agents. The hypothesis under investigation is that rapid decontamination can be achieved by the interaction of agent with silver metal clusters within zeolites coupled with subsequent photocatalytic excitation.

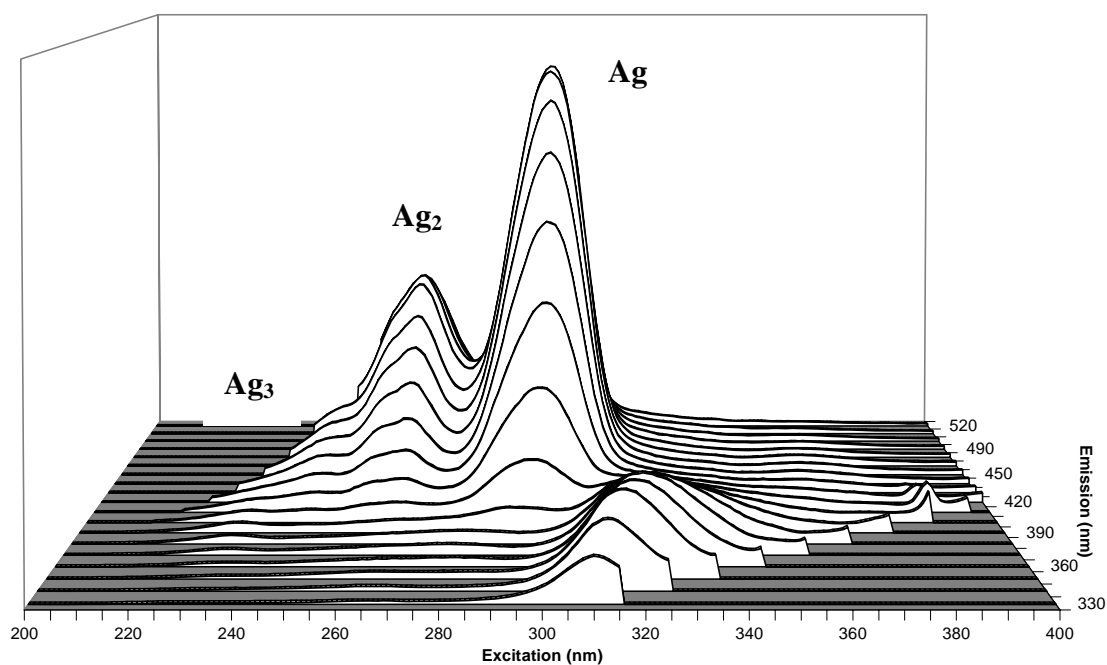
The research report includes the most important findings of the research and is divided into four sections: catalyst synthesis and characterization, reactor design, experiments involving nerve agent simulants, and experiments involving nerve agents.

### 1. Catalyst Synthesis and Characterization

Zeolites used in this study include purchased as well as synthesized material. All of the syntheses and ion exchange modifications were performed by University of Maine personnel in the Catalyst Synthesis Lab located in PI Howard Patterson's lab. Syntheses were performed using standard syntheses from the International Zeolite Association's Zeolite Handbook. Cation exchanges were performed using either  $\text{AgNO}_3$  or  $\text{Fe}_2\text{O}_3$  in  $\text{H}_2\text{O}$  and  $\text{NH}_4\text{OH}$ . All exchanges were conducted at 70 °C for 48h. The samples were washed with deionized water and dried at 85 °C for 24h. All the samples were then calcined at 500°C for 4h. Both x-ray diffraction (XRD) and Atomic Absorption spectroscopy (AA) were used to physically characterize the modified zeolites in order to verify their structure and measure the %Ag. Table I summarizes the different catalysts synthesized:

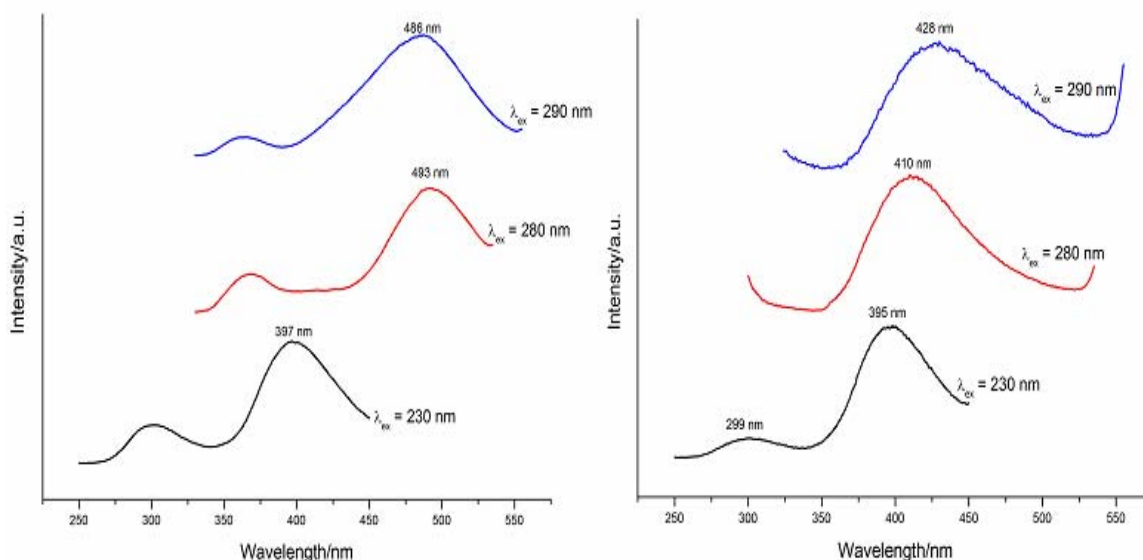
**Table 1. Zeolite catalyst types.**

<b>Zeolite</b>	<b>Exchange</b>	<b>Metals</b>
FAU	100	Cu/Ag (50/50)
FAU	0	None
FAU	25	Ag
FAU	100	Ag
FAU	100	Ag/Fe (50/50)
MCM-41	100	Ag
SOD	100	Ag
SOD	100	Ag/Fe (50/50)



**Figure 1. Three-dimensional excitation spectra of fully exchanged silver zeolite Y at 77K.**

In addition to the physical characterization by XRD and AA, the catalysts were also studied using solid state photoluminescence and transmission electron spectroscopy (TEM). The metal clusters in the inner pores and channels of the exchanged zeolites were primarily characterized using solid state photoluminescence. Three dimensional solid state luminescence data at low temperatures (77K) was used to probe the changes in the fluorophore with varying excitation wavelength. Figure 1 shows these changes in the luminescence of silver-exchanged Y-zeolite over varying excitation wavelengths. It has also been shown that the addition of a second cation species to the zeolite base can produce luminescence peaks that may be attributed to interactions between the two cation species, namely silver and iron oxide cations. Figure 2 shows the effect that the addition of Fe<sub>2</sub>O<sub>3</sub> has on the luminescence spectra of Y-zeolite.



**Figure 2. Solid state luminescence excitation spectra at 77K of (left) Ag-Y Zeolite and (right) Ag/Fe-Y Zeolite.**

TEM data was used specifically to investigate clustering induced by light exposure. This data together with luminescence data suggests that cluster formation within silver zeolites fills the pores of the zeolite they occupy. This finding is important when predicting which zeolite systems are more susceptible to silver leaching. The data suggests that MCM-41, ZSM-5 and MOR will have a higher incidence of leaching while higher Al content FAU and SOD would be more optimal choices for decontamination reactions.

## 2. Reactor Design

The design and installation of the remotely controlled and automated batch reactor for the laboratories of the Patterson Group at the University Maine and the design of a photo-activation device for the Edgewood Chemical and Biological Center was carried out by Applied Thermal Sciences, Inc.

The batch reactor at the University of Maine is a device that is used to handle a cuvette that contains measured amounts of zeolite and an aqueous solution. The device has five major components as follows: indexing (capability of moving the cuvette between locations); injecting a fluid into the cuvette; mixing the solution; illuminating the solution (open/close the laser shutter); and a graphical operator interface. There are two modes of operation, and the operator interface panel consists of push button to start the cycle, several registers to input necessary data to run the cycle, a flashing or blinking light signaling the end of the cycle and an abort push button. The device is placed in a “box” to eliminate stray light and allow for coupling to the UV tunable laser. Double redundant interlocks have been placed on access doors and panels to ensure the device is closed

prior to operation. Figure 3 shows the test apparatus set up in the catalysis synthesis laboratory at the University of Maine. This test apparatus was delivered to the University of Maine in November, 2004.



**Figure 3. Automated batch reactor aligned with an Optronic, Inc. tunable UV laser source.**

The photo-activation device (PAD) developed for the ECBC by Applied Thermal Sciences was designed based on the desires of the ECBC staff and requirements of ECBC protocol. ECBC requires positive control of chemical agents at all times, and therefore automated mechanisms cannot be utilized. To ensure consistency of the exposure time to the UV source, an automated timing device was implemented. A manual override switch is included to shut the lamp off in case of emergency. Additionally, to prevent accidental UV exposure, an interlock system is included that disables the UV lamp unless the system is properly assembled. When the system was designed, ATS engineers did not know what frequencies were most effective or the amount of time the metallic zeolite should be exposed to the UV source. Because of this, a broadband UV source was selected. The timer also has a wide range of settings from a few seconds to hours.

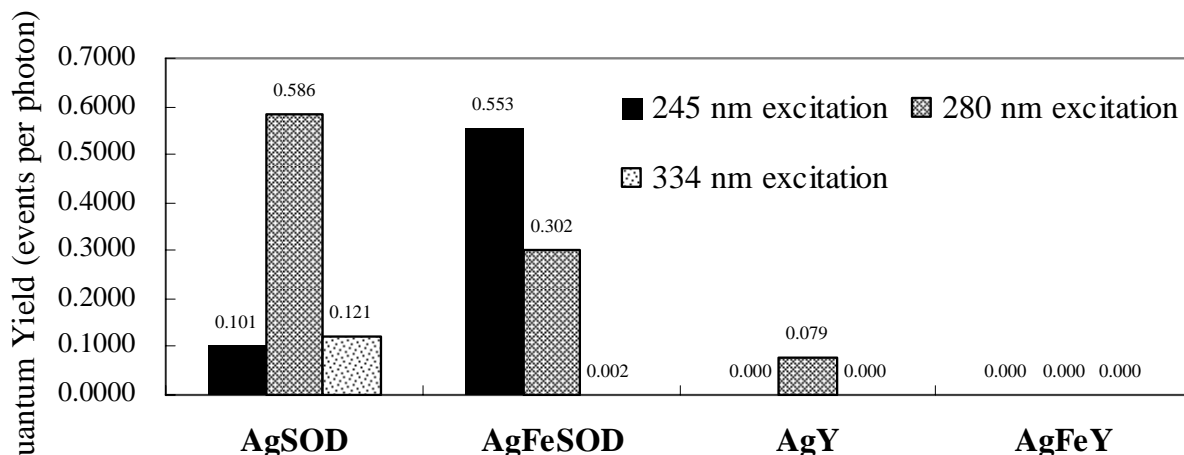


**Figure 4. Assembled photo-activation device.**

The PAD is designed to safely provide a stable and repeatable UV light source for evaluation of a UV photo catalyst for the decontamination of nerve agents. The pulsed xenon UV light source operates at 200Hz over a spectrum of 220nm to 750nm. Additional design features include a control box that is operable with bulky gloves and safety interlock switches to prevent accidental operation of the UV lamp. Figure 4 shows the complete photo activation device, which consists of three main components: the control box, the UV xenon lamp, and the illumination chamber.

### **3. Experiments Involving Nerve Agent Simulants**

For the catalyst performance studies carried out at the University of Maine, a nerve agent stimulant was used for the experiments. This stimulant was carbaryl, a common pesticide containing a carbamate functional group that is similar to the functional groups of several nerve gases. All these reactions were carried out using an Opatok, Inc. Opolette UV tunable laser system and automated batch reactor. Actinometry was carried out for each of the three UV wavelengths used in the experiments (245 nm, 280 nm and 334 nm) using an IUPAC accepted azobenzene actinometer<sup>1</sup> in order to determine the quantum yields of the catalyst performance experiments. The wavelengths of UV radiation used in this research were chosen in order to correspond with wavelengths that have known quantum yields for the azobenzene actinometer. Emission scans of each diluted aliquot sample were carried out on a Joriba-Yvon Fluorolog 3 luminescence spectrometer, with excitations at 270 nm and emission scans between 300 nm and 360 nm. For the hydroxyl radical scavenger experiment using Ag-SOD as a catalyst and a laser wavelength of 280 nm, the experimental method mentioned previously was used, with the only difference



**Figure 5. Averaged quantum yields for each of the synthesized catalysts for three different excitation wavelengths.**

being the addition of excess (68.4 mg)  $\text{NaHCO}_3$  (Sigma-Aldrich) to the reaction prior to exposure to the laser. For the deuterated water experiment using Ag-SOD as a catalyst and a laser wavelength of 280 nm, the original experimental method mentioned previously was used, with the only difference being the use of a 50 ppm solution of carbaryl in  $\text{D}_2\text{O}$  (Sigma-Aldrich, 99%).

The results of the initial catalyst performance experiments are presented in Figure 5. Quantum yield calculations were based on measured reaction rates, actinometry measurements and first-order reaction equations. The first point that can be made from these results is that the sodalite-based catalysts performed much better than the Y zeolite-based catalysts. This result may be attributed to the existence of large cages in the framework of Y zeolite and the absence of cages in sodalite framework. Due to the framework of Y zeolite, most of the negatively charged sites where the catalytic metal clusters are located exist within the cages, and the size of a molecule of carbaryl is too large to fit into a cage within Y zeolite (which has a diameter at the mouth of the cage of  $13 \text{ \AA}$ ),<sup>2</sup> preventing the molecule from being in close proximity to the catalytic metal clusters. Sodalite does not have cages like Y zeolite, and so most of the catalytic metal clusters are deposited on the surface of the zeolite crystal, making the cluster accessible to target carbaryl molecules.

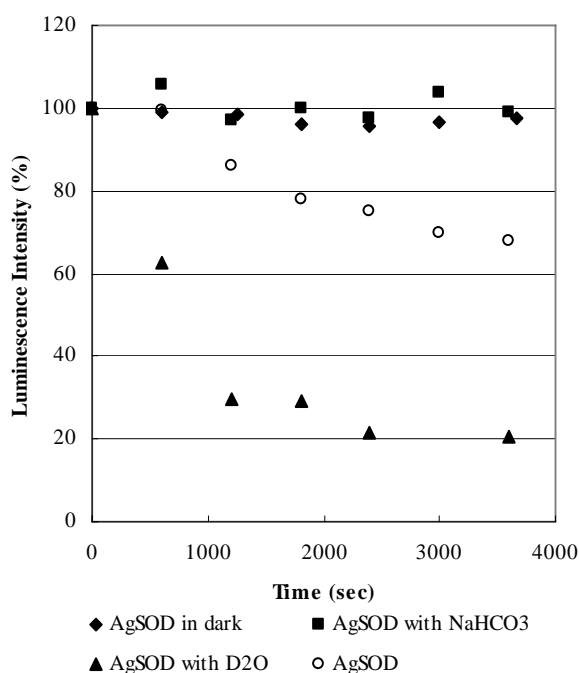
The second point that can be made from these results is that the quantum yields differed greatly depending on the wavelength of light used. Of the three wavelengths used, the 280 nm radiation was the most effective and the 334 nm radiation was the least effective, with one notable exception. This result corresponds nicely with the solid state luminescence spectra obtained of the catalysts, which have luminescence excitation maxima near 245 nm and 280 nm but have none near 334 nm. The activity shown by the catalysts at 280 nm excitation suggest that the majority of the metal clusters on the zeolite supports have sizes greater than dimers, and may be trimers of various geometries.

The third point that can be made from these results goes back to the notable exception that was referenced in the previous paragraph. This exception is the Ag/Fe-SOD catalyst, which has a much higher quantum yield value at 245 nm than it does at 280 nm. A



possible explanation for this phenomenon is the formation of catalytic metal clusters that have blue-shifted excitation maxima due to the presence of the  $\text{Fe}_2\text{O}_3$  dopant. However, this explanation does not agree with the solid state luminescence spectra of the catalyst, which shows no such blue shifting between Ag-SOD and Ag/Fe-SOD. This may be because not all of the  $\text{Ag}^+$  exciplexes in Ag-SOD interact with the  $\text{Fe}_2\text{O}_3$  dopant. This means the exciplexes that do interact with the  $\text{Fe}_2\text{O}_3$  dopant may form clusters that show a new excitation peak near 245 nm that was not initially detected by the solid state luminescence experiments. With the exception aside, the addition of  $\text{Fe}_2\text{O}_3$  to the Ag-SOD and Ag-Y catalysts did not enhance the quantum yields on the whole. This may be because while  $\text{Fe}_2\text{O}_3$  is interacting with the  $\text{Ag}^+$  clusters (which is shown by the solid state luminescence spectra in Figure 2), the oxide molecule may be blocking target molecules and reactants from interacting with the clusters. This applies especially to the Y zeolite-based catalyst at 280 nm, which exhibits a small amount of activity when doped with just  $\text{Ag}^+$  but shows no activity when doped with both  $\text{Ag}^+$  and  $\text{Fe}_2\text{O}_3$ . This theory coincides with previous research, which claims that the addition of a second metal to a catalytic metal cluster may suppress the absorption of reactants onto the support material.<sup>3,4</sup>

The results of the hydroxyl radical scavenger and deuterium-doped solvent experiments are shown in Figure 6. These results suggest a mechanism for carbaryl decomposition by silver clusters that is different than what has been previously proposed.<sup>5</sup> The experiment



**Figure 6. Luminescence intensity of carbaryl over time in the presence of Ag-sodalite and 280 nm excitation under differing conditions.**

that does not include the 280 nm excitation shows very little activity; this suggests that UV light is a necessary reagent needed for the decomposition of carbaryl using Ag-doped catalysts. The existence of a small amount of activity may be due to ambient light entering the batch reactor. The experiment that included an excess of sodium bicarbonate, a known hydroxyl radical scavenger,<sup>6</sup> showed even less activity than the dark reaction. This finding suggests that hydroxyl radicals are being formed in the solution by the excited metal clusters and it is the radicals that ultimately interact with the carbaryl molecules and begin the process of decomposition. This means the excited metal clusters themselves may interact primarily with nearby water molecules and remove protons from the molecules.

This immediately raises the question as to why the Y zeolite catalysts did not exhibit higher quantum yields if size exclusion by the Y zeolite cages was no longer a

factor. This question may be answered by the catalyst performance experiment with the Ag-SOD catalyst that used D<sub>2</sub>O instead of H<sub>2</sub>O as a solvent. Hydroxyl radicals with deuterium have much longer lifetimes than hydroxyl radicals with hydrogen, and with that in mind, the carbaryl molecules have a much larger window to react with the radicals with D<sub>2</sub>O as a solvent. The results of the D<sub>2</sub>O solvent experiments shown in Figure 6 strengthen this theory. The quantum yield of the Ag-SOD catalyst at 280 nm excitation in D<sub>2</sub>O is nearly six times the quantum yield of the same experiment in H<sub>2</sub>O. This gives further evidence to a mechanism that involves hydroxyl radical formation by the excited metal clusters. It may also explain why hydroxyl radicals from H<sub>2</sub>O that may be formed by Y zeolite-based catalysts do not significantly interact with the carbaryl molecules: the lifetimes of the radicals may be too short to allow for the time of diffusion of the radical from the zeolite cage.

#### 4. Experiments Involving Nerve Agents

Catalytic performance studies using the synthesized catalysts and genuine nerve agents were carried out by the Edgewood Chemical and Biological Center. The purpose of the studies were to determine the reduction in HD of Ag-exchanged samples compared to the parent material and for samples activated with UV light compared to non-activated samples.

Extractions of reaction solutions were performed in small glass Petri dishes to eliminate some solvent compatibility issues. Tests were performed by placing five 2-μL drops of agent on the bottom of the Petri dish. A mass of 0.2 g of catalyst or zeolite powder was poured over the top of the drops. The dish was covered and either placed in the ATS photo-activation device, or was left in the hood for a period of 20 minutes. Following this exposure time, the dish was extracted with 20 mL of chloroform. The resulting mix was stirred with a pipette tip, and then filtered with a glass fiber filter into a GC vial. The samples were then analyzed using a Gas-Chromatography Flame Ionization Detector (GC-FID).

Table 2 provides the results of the experiments done at ECBC.

**Table 2. Nerve Agent Breakdown Results**

<b>Material</b>	<b>HD Remaining</b>	<b># Runs</b>	<b>HD Remaining</b>	<b># Runs</b>
MCM-41	93%	1	N/A	0
Ag-MCM-41	63%	1	N/A	0
SOD	64%	3	67%	3
Ag-SOD	113%	1	90%	3
FAU	90%	2	76%	2
Ag-FAU	57%	1	62%	1
Ag-Y Zeolite (Purchased)	55%	4	65%	4

The summary of these results acquired from the ECBC are as follows:

- Ag-zeolite purchased from Aldrich and SOD parent had sufficient sample to enable several tests. The SOD parent showed a ~40% reduction in HD concentration without UV activation. UV activation did not provide measurable improvement. The commercial Ag-zeolite showed ~35% reduction in HD concentration without UV activation. An additional 10% reduction was observed with UV activation.
- MCM-41
  - The Ag-MCM-41 structure type showed a much greater reduction in HD concentration than the parent MCM (~40 % reduction versus ~10 % reduction in parent material).
  - The effect of UV activation was not tested due to insufficient sample quantity.
- SOD
  - Amongst the four replicates, the parent material showed a greater reduction of HD concentration than the Ag-SOD (~40 % reduction versus ~20 % reduction in Ag material).
  - No observable difference was noted for UV activated SOD versus unactivated. Unactivated Ag SOD caused a slightly greater reduction in HD concentration.
- FAU
  - The parent material showed no observable reduction in HD concentration for three of four replicates. The Ag FAU showed a greater reduction of HD concentration (~40 % reduction).
  - No observable difference was noted for UV activated FAU versus unactivated FAU. No observable difference was noted for UV activated Ag FAU versus unactivated Ag FAU.
- Ag-Zeolite (Aldrich)
  - In five of the six replicates, Ag-Zeolite showed a 50 % reduction in HD concentration.
  - No observable difference was noted for UV activated Ag Zeolite versus unactivated Ag Zeolite.

## **Publications and Reports Resulting From Research**

2004 Technical Report on Grant W911NF-04-1-0246, submitted to ARO

2005 Technical Report on Grant W911NF-04-1-0246, submitted to ARO

Gomez, Robert S.; Yson, Renante L.; Lu, Haiyan; Li, Xiaobo; Patterson, Howard H. "A mechanistic study of the UV photodecomposition of carbaryl in the presence of homometallic and heterometallic zeolites." Submitted to the *Journal of Physical Chemistry B: Catalysis*. In review.

Kanan, Sofian M.; Kanan, Marsha C.; Patterson, Howard H. "Photoluminescence spectroscopy as a probe of silver doped zeolites as photocatalysts." *Curr. Opin. Solid State Mater. Sci.* **2004** 7, 443.

Kanan, Sofian M.; Kanan, Marsha C.; Patterson, Howard H. "Silver nanoclusters doped in X and mordenite zeolites as heterogeneous catalysts for the decomposition of carbamate pesticides in solution." *Research on Chemical Intermediates*. In press.

Yson, Renante L.; Gomez, Robert S.; Lu, Haiyan; Patterson, Howard H. "Nanoclusters of silver doped in zeolites as photocatalysts." *Catalysis Today*. In press.

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John Anderson, M.S. candidate, Chemistry

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Donald Bragg, M.S. candidate, Mechanical Engineering

Robert S. Gomez, Ph.D. candidate, Chemistry

Susan MacKay, Ph.D., adjunct faculty, Department of Chemistry

Howard H. Patterson, Ph.D., P.I., Department of Chemistry

Brian Schaefer, M.S., Chemistry (earned during grant activation period)

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